

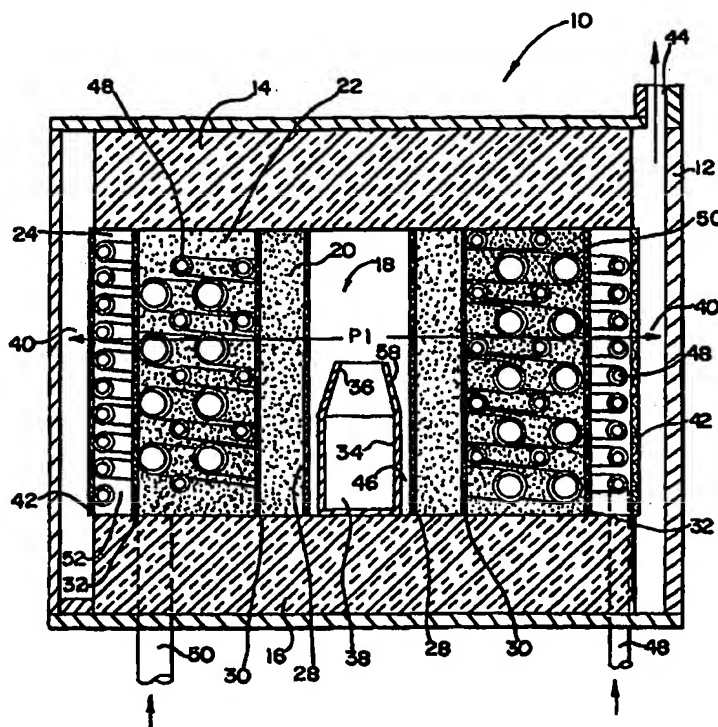


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<b>(21) International Application Number:</b> PCT/US99/00833 <b>(22) International Filing Date:</b> 13 January 1999 (13.01.99) <b>(30) Priority Data:</b> 09/006,727 14 January 1998 (14.01.98) US <b>(71) Applicant:</b> ARTHUR D. LITTLE, INC. [US/US]; 25 Acorn Park, Cambridge, MA 02140-2390 (US). <b>(72) Inventors:</b> BENTLEY, Jeffrey, M.; 20 Landmark Road, Westford, MA 01886 (US). MITCHELL, William, L.; 111 Oakley Road, Belmont, MA 02178 (US). CLAWSON, Lawrence, G.; 7 Rocky Brook Road, Dover, MA 02030 (US). CROSS, James, C., III; 96 County Road, Ipswich, MA 01938 (US). <b>(74) Agents:</b> MORNEAULT, Monique, A. et al.; Wallenstein & Wagner, Ltd., 311 South Wacker Drive - 5300, Chicago, IL 60606 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** REACTOR FOR PRODUCING HYDROGEN FROM HYDROCARBON FUELS**(57) Abstract**

A reformer reactor (10) for producing a hydrogen-rich gas includes a first zone (18), a second zone (20), a third zone (22), a fourth zone (24) and a product gas collection space (40). The zones are sequentially adjacent. A flow path P1 is provided for directing flow of a reaction stream in diverging directions from the first zone (18) into the second zone (20), the flow of the reaction stream continuing in the same general diverging directions through the second zone (20) and into and through the third and fourth zones (22, 24). Directing the flow in diverging directions permits flow into and through a zone over more than just a single cross-sectional geometry of the zone or a single cross section of the flow path transverse to the direction of flows. This configuration can be used to require a lower pressure for flowing the reaction stream so as to reduce the parasitic requirements of the reactor. This configuration can also be used to increase throughput of the reactor.



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REACTOR FOR PRODUCING HYDROGEN FROM  
HYDROCARBON FUELS

DESCRIPTION

Technical Field

The present invention is related to reactors which liberate hydrogen from hydrocarbons by reforming reactions, and more particularly to novel: reactor geometries; reaction zone relationships; reaction stream flow paths; heat transfers; and, reactant feed systems.

Background of the Invention

Reforming hydrocarbons including alcohols to produce hydrogen is well known and many reactors have been constructed for this purpose, for example see U.S. Patent No. 5,458,857 to Collins et. al., and U.S. Patent No. 5,030,440 to Lywood et. al. Reforming reactions are also known to be coupled in a reactor process stream with partial oxidation reactions (e.g., autothermal reforming) and shift reactions.

One important use of the hydrogen liberated by reforming is the production of electricity in an electrochemical fuel cell which uses the hydrogen as a fuel. A significant advantage of producing hydrogen in this manner is that reactors can be coupled directly to a fuel cell and can be controlled to produce hydrogen as needed based upon a fuel cell's load demands. The storage and handling of reactants to produce the hydrogen is easier, safer and more energy-dense than stored bulk, hydrogen.

Recently, a commercial market has emerged for clean, portable, electric power generation from fuel cells.

To enhance portability of a fuel cell it is advantageous that it be compact and lightweight. Accordingly, a reactor to supply hydrogen to the fuel cell must also be compact and lightweight. The reactants on which a hydrogen-producing reactor operates should be readily available, to foster acceptance and wide usage. A preferable reactant fuel should be easily storable to minimize fuel storage volume.

However, problems exist with conventional reactor designs with regard to meeting the above-stated needs of portability and compactness. A small system employing conventional technology is anticipated to have increased heat losses relative to reactant fuel throughput. This would result in inherently lower efficiencies than conventional systems used for larger power outputs.

Also, parasitic power requirements, which are generally dominated by air or hydrocarbon fuel compressors, blowers or pumps, can reduce the usable total energy-producing potential of the system sufficiently to make such a system unattractive for utilization in most portable applications.

One cause for the need of parasitic power is the total pressure drop of a reaction stream through a reactor having two or more zones where reactions occur. The pressure drop (or looked at another way the pressure required to drive a reaction stream through the reactor) results in-part, from the internal geometries and reaction stream flow paths provided by these conventional reactors.

Some have provided reactors which direct the reaction stream along tortuous flow paths, such as through helical zones, or by changing (most often, completely reversing) flow directions in one zone versus another.

Also, the reaction stream may be transferred from one zone to another through some form of constricting geometry such as an orifice or annular transition zone, for example, see Collins et. al. and Lywood et. al. These types of flow  
5 paths, which among other things, are designed to effect advantageous heat transfers, increase pressure requirements for the system.

Others have provided reactors where the reaction stream flow path from zone to zone is more direct and is  
10 generally in a single direction traversing zone to zone. However, these configurations limit flow throughput by providing a flow path area only as large as a single cross-sectional area of the reactor zone, for example see U.S. Patent Nos. 4,822,521 to Fuderer; 4,789,540 to Jenkins;  
15 4,716,023 to Christner; 4,522,894 to Hwang et. al.

The present invention has been provided to cure the above deficiencies in the art and to provide other advantages to meet the needs of the market for the production of hydrogen for general purposes and in  
20 particular as a source of fuel for fuel cells.

#### Summary of the Invention

The present invention provides a reformer reactor which liberates hydrogen from hydrocarbon fuels including alcohol, with carbon dioxide, water, and carbon monoxide as  
25 by-products. The hydrogen produced by the reactor, among other things, can be electrochemically combined with oxygen in a fuel cell to produce electric power.

Preferred embodiments of the invention were developed primarily for portable power applications  
30 requiring a relatively small chemical processing system. Nevertheless, the same principals applicable to the preferred embodiments of the present invention are believed

to provide advantages for larger systems for producing hydrogen for its many purposes in industry.

For example, the following principles of structure and function contemplated by the present invention are believed to apply generally to reactors for reforming hydrocarbon fuels to make hydrogen: internal and overall reactor geometry permitting reduced pressure requirements for reaction stream flow; synergistic relationship between reaction stream flow path and overall thermal losses of the reactor; reduction of parasitic power requirements; synergistic heat transfers between reaction stream flow paths and reactant feed stream preheat requirements; optimization of heat transfer while minimizing flow restrictions on the reaction stream; and, the provision of thermal gradients across catalyst beds for optimization of catalyzed reactions. According to the invention one or more of these principles may be applied to, or result from, the following novel structures.

A reformer reactor according to the invention includes at least a first zone and a second zone adjacent the first zone. A flow path is provided for directing flow of a reaction stream in diverging directions from the first zone into the second zone. The flow path of the reaction stream is such that the reaction stream continues in the same general diverging directions through the second zone as it did entering the second zone.

With a flow path according to the present invention, configured to permit flow in diverging directions and continuing in the same directions through each desired zone, a lower pressure is required for flowing the reaction stream. This reduces the parasitic requirements of the reactor. Conversely, if desired, the

same configuration will permit a higher throughput for any given system power ascribed to flowing reactants.

In another respect, directing the flow in diverging directions also permits flow into and through a zone over more than just a single cross-sectional geometry of the zone or a single cross-section of the flow path transverse to the direction of flows. For example, in reactors where flow is axial, in one direction, flow from one zone to the next is limited to a flow path of no larger cross-sectional area than the cross section (taken transverse to the direction or flow) of the zone itself. If, however, according to the principles of the present invention, the flow path is directed from a first zone towards two second zones, one on either side of the first zone, the flow could be directed at 180 degree divergent directions down the same axis. This would effectively double the cross section of the flow path into and through the second zones. Accordingly, the pressure drop would decrease for the same level of throughput, or the throughput could be doubled for the same pressure.

Flowing the reaction stream over larger areas (larger cross section) permits a lower flow rate for any given throughput. This advantageously can be used to achieve a longer residence time for the reactants in any given zone (at any given throughput) so as to increase the extent of reaction in the zone and thus, increase yields.

The principles of the invention are particularly advantageous with zones having cylindrical, hemispherical, or spherical geometries. In such cases the flow path can be directed in diverging radial directions away from the first zone and into and through subsequent zones. However, the same principles are believed to apply to other

geometries including those having rectilinear and polygonal zone geometries.

To assist flow in diverging directions over large cross-sectional areas of a zone, the boundaries of the zones are made permeable to the flow of a reaction stream. A preferred way to accomplish this is to provide permeable partitions separating the various zones. Such partitions can have a plurality of spaced openings to permit the flow of the reaction stream therethrough in diverging directions. For example, one preferred partition is a screen mesh. The openings can also be sized and spaced so as to "partition" and regulate flow from one zone to the next. Partitioning in this manner can assist in avoiding having larger amounts of flow through certain areas of the zone than others. This increases yield and may reduce hot spots in the zones (such as those containing a catalyst), where exothermic reactions occur. The partitions can also serve to captivate granular catalysts in desired zones.

In a preferred reactor according to the invention, a partial oxidation reaction vessel is located within a first zone. The vessel has an opening for emission of partially oxidized hydrocarbons into the first zone; and, the number, size, and spacing of the partition openings are selected to control the flow rate and uniformity of the reaction stream from the first zone and into the second zone. The partition may also be constructed of material composition, thickness, and finish selected to provide a desired degree of thermal insulation or reflectivity, to assist in controlling heat transfer from the partial oxidation vessel into the second zone.

While it is contemplated that a reactor according to the invention may have any number of zones containing



catalysts for catalyzing a desired reaction within a zone, a preferred embodiment specifies that a second zone contains a catalyst suitable for catalyzing a steam reforming reaction in the reaction stream, a third zone  
5 contains catalyst suitable for catalyzing a high-temperature shift reaction in the reaction stream, and a fourth zone includes a catalyst suitable for catalyzing a low-temperature shift reaction in the reaction stream.

According to another aspect of the invention a  
10 reactor is provided with means for heat exchange between heat generating portions of the reaction stream and a reactant feed stream prior to entry of the reactants into a first zone. The means is preferably disposed in at least one of a second, third, or subsequent zones so as to  
15 utilize heat from the reaction stream flowing therethrough to preheat the feed stream. Preferably the means is disposed in direct contact with a granular catalyst in at least one of the zones so as to utilize heat from the reactant stream and the heat from the catalyst to preheat  
20 the feed stream.

According to another aspect of the invention, the means for heat exchange with a reactant feed stream also includes a means for regulating the heat exchange in such a way as to achieve a desired in the catalyst and reaction  
25 stream temperature across the zone.

According to another aspect of the invention, a reactor includes a means for flowing oxygen to a first zone and a means for flowing a hydrocarbon fuel to be oxidized to the first zone. A means is provided for cooperating the  
30 means for flowing oxygen and the means for flowing fuel such that the flow of fuel assists the flow of oxygen to reduce parasitic power requirements in providing oxygen to

the first zone. Preferably, the means for cooperating includes joining the fuel flow into the oxygen flow downstream of a source of the oxygen (preferably air) and flowing the fuel at a higher velocity than a velocity of  
5 the oxygen upstream of joining the fuel flow.

According to certain principles of the invention, advantageous reactor constructions can be provided by a vessel having a first zone for containing a reaction stream, a collection space for collecting product gas, and  
10 one or more intermediate zones are interposed between the first zone and the collection space. A means is provided for directing the reactant stream from the first zone to the collection space, primarily in directions coinciding with the directions of a substantial portion of the overall  
15 heat flux out of the vessel. Such a design is again most advantageous where all of the zones are arranged as nested; coaxial cylinders; hemispheres; or, spheres, and the vessel includes sufficient thermal insulation at appropriate areas such that heat flux and accordingly the reactant flow, is  
20 primarily radially outward from the first zone to the collection space.

According to the invention it is most advantageous with nested zones to provide a boundary between each zone, which is permeable to the reaction stream so as to permit  
25 flow between relevant zones to and through each subsequent zone through the respective boundaries therebetween.

Other advantages and aspects of the present invention will become apparent upon reading the following description of the drawings and detailed description of the  
30 invention.

#### Brief Description of the Drawings

FIG. 1 is a view of a cylindrical reformer reactor 10 in vertical cross section;

FIG. 2 is a schematic view of a horizontal cross section of reactor 10;

5        FIG. 3 is partial cross section view of a jet ejector 54 utilized in connection with reactor 10;

FIG. 4 is a schematic view of a vertical cross section of a hemispherical reactor 60;

10       FIG. 5 is a schematic view of a vertical cross section of a spherical reactor 76; and,

FIG. 6 is a schematic view of a vertical cross section of an alternate cylindrical reactor 96.

15       FIG. 7 is a schematic view of a vertical cross section of another embodiment of a cylindrical reactor 122.

#### Detailed Description

While this invention is susceptible of embodiment in many different forms, there is shown in the drawings and will herein be described in detail preferred  
20       embodiments of the invention with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the broad aspect of the invention to the embodiments illustrated. It should also be  
25       understood that not every disclosed or contemplated embodiment of the invention needs to utilize all of the various principles disclosed herein to achieve benefits according to the invention.

30       FIG. 1 discloses a reformer reactor 10 which is a miniature chemical processing system that liberates hydrogen from hydrocarbon fuels including alcohols, with carbon dioxide, water, and carbon monoxide as by-

products. The hydrogen can be used for any use for which hydrogen is desired. However, reactor 10 is particularly useful for providing hydrogen to be electrochemically combined with oxygen in a fuel cell to produce portable electric power.

One design emphasis for reactor 10 is portability. Specifications achieved by the design are compactness, lightweight, operation on readily-available and easily-storable fuel (e.g., propane, alcohols, gasoline), near-atmospheric operating pressure, low overall pressure drop, and a firing rate of 250-500 Watts (LHV). The reactor 10 is sized for 100 Watts of delivered power when integrated as a fuel cell power system.

The reactor 10 has a metal cylindrical reactor housing 12 substantially capped at its axial ends by insulating slabs 14 and 16. In the housing 12, are sequentially adjacent, first, second, third, and fourth zones 18, 20, 22, and 24. As schematically shown in FIG. 2, the four zones 18, 20, 22, and 24 are nested cylinders. At the boundaries between the zones are permeable partitions in the form of wire mesh screens 28, 30, and 32. Referring back to FIG. 1, a partial oxidation reaction vessel 34 is located within the first zone 18. The vessel 34 has a frustoconical upper portion 58 having an opening 36. In other embodiments the portion 58 could be other shapes, such as, cylindrical or frustospherical.

In the basic mode of operation of the reactor 10, reactants, hydrocarbon fuel, steam and air are flowed as a reaction stream into the vessel 34 through inlet 38 where a partial oxidation is effected on the reaction

stream to produce hydrogen and carbon monoxide predominantly. Some methane is produced as well and, depending on the reactant fuel, small amounts of waste constituents, such as gaseous sulphur compounds. The  
5 reaction stream exits opening 36 of vessel 34 and flows into, and fills, the first zone 18. The reaction stream is directed in diverging directions from the first zone 18 and into the second zone 20 along a flow path P1 (exemplary diverging radial directions indicated by  
10 arrows P1 FIGS. 1 and 2). The flow of the reaction stream continues in the same general diverging radial directions through the second, third and fourth zones 20, 22 and 24 all along flow path P1. Flow path P1 permits flow from an area 360° around each zone 18, 22 and 24 and  
15 over their entire axial lengths. The reaction stream then passes through a cylindrical wire mesh screen 42 to enter a cylindrical (annular) collection space 40 where hydrogen can be suitably collected and exited such as by exit tube 44. The width of the annular gas collection  
20 space 40 is chosen to sufficiently minimize pressure losses associated with flow consolidation and restriction.

In operation, when the reaction stream exits the partial oxidation vessel 34 it is initially flowing  
25 axially with respect to the first zone 18. This is the point at which the flow begins its transitions to radially diverging directions. However, the screen 28 has a mesh open area and sheet thickness selected to permit enough back-pressure so that the reaction stream  
30 fills the first zone 18. The back-pressure is still low enough so as not to impair flow efficiency or unduly increase parasitic energy loss. This is done to achieve

near-uniform flow distribution out of the first zone 18 including from an annular area 46 surrounding the partial oxidation vessel 34. The screen 28 can also be constructed of material composition, thickness, and finish to assist in controlling the amount of heat transferring from the exothermal partial oxidation reaction vessel 34. For example, the finish could assist in reduction of radiant heat losses from the reaction vessel 34 and the first zone 18. Also, the flow partitioning provided by the open space along with the thermal conductivity of material can assist with even distribution of conductive and convective heat transfer into the second zone to reduce hot spots therein. In some embodiments the partitions themselves could be coated with catalyst to improve completeness of reaction.

Hydrocarbon fuel is fed to the reactor 10 through tube 48 which inside the reactor 10 is formed into three helical sections or passes as it approaches the inlet 38 of vessel 34. Optionally, two-phase steam/water can be fed with the fuel into tube 48. An oxygen-containing gas, preferably air, is fed to the reactor 10 through tube 50 which inside the reactor 10 is formed into two helical passes as it approaches the inlet 38 of vessel 34. The multiple passes of the helical portions of tubes 48 and 50 are afforded by U-bends (not shown) joining the helical runs of tube 48. Preferably the inlet of the tubes 48 and 50 have an optimized maximal diameter and the outlets have an optimized minimal diameter.

The second zone 20 contains a catalyst suitable for catalyzing a steam reforming reaction in the reaction stream. Preferably, the steam reforming catalyst includes nickel with amounts of a noble metal, such as

cobalt, platinum, palladium, rhodium, ruthenium, iridium, and a support such as magnesia, magnesium aluminate, alumina, silica, zirconia, singly or in combination. Alternatively, the steam reforming catalyst can be a  
5 single metal, such as nickel, or a noble metal supported on a refractory carrier like magnesia, magnesium aluminate, alumina, silica, or zirconia, singly or in combination, promoted by an alkali metal like potassium.

The third zone 22 contains a catalyst suitable  
10 for catalyzing a high-temperature shift reaction in the reaction stream. Examples of suitable high temperature shift catalysts are those that are operable at a temperature in the range of between about 300°C and about 600°C. Preferably the high-temperature shift catalyst  
15 includes transition metal oxides, such as ferric oxide ( $\text{Fe}_2\text{O}_3$ ) and chromic oxide ( $\text{Cr}_2\text{O}_3$ ). Other types of high temperature shift catalysts include iron oxide and chromium oxide promoted with copper, iron silicide, supported platinum, supported palladium, and other  
20 supported platinum group metals, singly and in combination.

The fourth zone 24 contains a catalyst suitable for catalyzing a low-temperature shift in the reaction stream. An example of a suitable low temperature  
25 modifying catalyst are those that are operable at a temperature in a range of between about 150°C and about 300°C. Preferably, the low temperature modifying catalyst includes cupric oxide ( $\text{CuO}$ ) and zinc oxide ( $\text{ZnO}$ ). Other types of low temperature shift catalysts  
30 include copper supported on other transition metal oxides like zirconia, zinc supported on transition metal oxides or refractory supports like silica or alumina, supported,

supported ruthenium, supported rhenium, supported palladium, supported rhodium and supported gold.

Preferably, the high- and low-temperature shift catalysts are in granular form and the tubes 48 and 50 are buried in the catalyst granules. The diameters of the tubes 48 and 50 are individually selected to optimize heat exchange with the reaction stream and the catalysts while properly managing pressure drop.

Preferably the fuel/steam is delivered under pressure which permits a reduction in diameter (increased pressure drop) in the tube 48. The vapor pressure of gaseous fuels such as propane, fuel can be used to induce fuel flow. In the case of alcohols, a mini-pump or auxiliary heating to increase vapor pressure is required to establish driving pressure. It is preferable that the air not be delivered under pressure because of the parasitic power required to pressurize the air flow. Thus, the tube 50 can afford less pressure drop than tube 48 and therefore it has a relatively larger diameter.

As disclosed in FIG. 3, the fuel steam and air feeds are preferably mixed inside the reactor housing 12 (not shown in FIG. 1) by a means for cooperating the means for flowing oxygen and the means for flowing fuel such that the flow of fuel assists the flow of oxygen. In the preferred embodiment a jet ejector 54 is provided such that the fuel-steam issues at a higher velocity from a smaller-diameter tube, such as a nozzle 56, disposed in the axial center of a portion of the air tube 50. As mentioned before, this reduces the amount of work being done to deliver the requisite amount of air because jet ejector 54 pulls the air, thereby minimizing requirements for upstream pressurization. The mixing location (i.e.,



the location of jet ejector 54) is chosen to minimize the chance of ignition of reactants before they reach the vessel 34, while ensuring satisfactory fuel/steam/air mixing.

5           After mixing, the reactants are directed to the inlet 38 of the vessel 34. The reactants are directed tangentially around the cylindrically-shaped vessel 34 so as to induce a swirling flow during combustion. This leads to better mixing, thermal homogeneity, and in  
10   general, better performance. For example, the swirling provides a higher flame stability and less tendency for carbon soot formation. The vessel 34 is sized to accommodate the requirements of 250-500 Watt thermal input (LHV). A frustoconical reducer 58 of the vessel  
15   34, serves to maintain flame stability internally, as well as enhance the view factor for radiative heat exchange with the surroundings. Using gaseous fuels or alcohols, the reaction stream exiting the exit 36 of the vessel 34 will generally consist of 18-24 volume percent  
20   hydrogen gas, 8-12 volume percent carbon monoxide gas, and 2-3 volume percent methane gas, on a dry basis.

          As the reaction stream flows through the second zone 20, the steam-reforming catalyst catalyzes a steam reforming of residual fuel. This increases hydrogen  
25   production efficiency. The level of methane after this stage will be generally on the order of 1 percent or less, with the hydrogen and carbon monoxide levels having increased accordingly.

          As the reaction stream flows through the third  
30   zone 22, the high-temperature shift catalyst accelerates the water/gas-shift reaction in the temperature range of roughly 400°C-650°C. These high temperatures lead to

increased chemical kinetics, but lead to less favorable equilibrium, that is, higher carbon monoxide to hydrogen ratios. The water/gas-shift reaction is exothermic. As the shift reaction progresses, favorable equilibrium is increasingly more desirable than higher kinetic rate. In other words, at the inner radius of the third zone 22, high temperatures and corresponding high kinetic rates are desirable for a given flow throughput requirement. However, as the stream continues through the catalyst, a lower temperature with more favorable chemical equilibrium to produce hydrogen and corresponding lower kinetics is desirable.

Thus, it is important that the temperature of the third zone 22 have a temperature gradient decreasing in the direction of reaction stream flow across the third zone 22 in order to optimize performance. This is addressed in reactor 10 by utilization of the countercurrent heat exchange accomplished by tubes 48 and 50 carrying the reactant feed streams. The air/fuel/steam feed streams are cold with respect to reaction stream and catalyst in the third zone 22, thus balancing the reaction stream heat rejection requirement.

The composition of the reaction stream gases upon leaving the third zone 22 is 30-36 volume percent hydrogen and nominally 1 volume percent carbon monoxide.

As the reaction stream flows through the fourth zone 24, the low-temperature shift catalyst, catalyzes essentially the same reactions as in the third zone 22. Because this reaction is also exothermic, and should preferably be conducted at the lower temperatures of 250-450°C, heat exchange is necessary to cool the fourth

zone. This cooling is effected by the first (radially outer-most) helical pass of the fuel/steam tube 48.

FIGS. 4 - 6 disclose other exemplary reactor geometries which will provide significant advantages according to the present invention.

FIG. 4 discloses a schematic cross section of a reformer reactor 60 with a hemispherical geometry. Nested, adjacent hemispherical zones 62, 64, 66, and 68 are provided in a geometry which permits a flow path P2 to direct reaction stream flow in diverging radial directions (along spherical coordinates) from the first zone 62, into and through the sequentially downstream zones 64, 66, and 68 and then into a collection space 70 defined by a hemispherical outer shell 72. A thermally insulating base 74 is provided to assist in the effort to have heat loss and reaction flow directed in the same directions.

FIG. 5 discloses a schematic cross section of a reformer reactor 76 with a spherical geometry. Nested, adjacent spherical zones 78, 80, 82, and 84 are provided in a geometry which permits a flow path P3 to direct reaction stream flow in diverging radial directions (along spherical coordinates) from the first zone 78, into and through the sequentially downstream zones 80-84 and then into a collection space 86 defined by a spherical outer shell 88. A spherical partial oxidation reaction vessel 90 (with openings, not shown) is provided at the center of the first zone 78. A fuel/steam tube 92 is disclosed schematically by hatched line. The tube has an inlet 94 and passes through the zones to effect the advantageous heat exchanges disclosed with respect to

reactor 10. Similar preheat tubes could also be provided for air/oxygen.

FIG. 6 discloses a schematic cross section of a reformer reactor 96 with a cylindrical geometry such as reactor 10. However, reactor 96 has a first zone 98, which is adjacent to two second zones 100, 102, which are in turn adjacent to two third zones 104, 106, which are adjacent to two fourth zones 108, 110. Each zone is cylindrical; thus the geometry permits a flow path P4 to direct reaction stream flow in 180 degree diverging axial (rather than radial) directions from the first zone 98, into and through the sequentially downstream zones 100-110 and then into collection spaces 112, 114. As noted earlier, this diverging axial flow effectively doubles the throughput through the cylindrical cross section at a given pressure (or reduces the pressure required for a given throughput) as compared to conventional axial-flow reactor configurations. A partial oxidation reaction vessel 116 is provided at the center of the first zone 98 and could be fed reactants through counterflow, helically coiled, feed stream tubes such as tubes 48, 50 of reactor 10. A cylindrical reactor housing 118 is provided with a thermally insulating cover 120 to assist in coinciding the direction of significant portions of thermal loss with the direction of reaction stream flow.

In all of the reformer reactors 10, 60, 76 and 96: partial oxidation of a hydrocarbon fuel may be conducted outside the reactor and a partially oxidized hydrocarbon reaction stream be fed into the first zones 18, 62, 78, and 98. Optionally, a partial oxidation reactor such as vessels 34, 90, and 116 can be located within the first zones. Also optionally, a reaction

stream may be fed into the first zones 18, 62, 78 and 98, in a thermal condition for steam reforming therein. In all of the reformer reactors 60, 76 and 96, catalysts may be employed as desired in the various zones including the first zones 18, 62, 78 and 98.

One advantage of the geometries disclosed herein is that if a partial oxidation reaction is conducted in the first zone, the thermal energy of the exothermic reaction can be easily, and efficiently shared with a steam reforming reaction in an adjacent second zone. This is particularly advantageous where the second zone surrounds or substantially surrounds the first zone.

Tubes such as tubes 48, 50 of reactor 10 could be used in the same way in each reactor 10, 60, 76 and 96, to achieve the same heat exchanges for preheating reactants and for providing an advantageous thermal gradient across catalyst zones. All of the boundaries between zones in each of the reactors 60, 76, and 96 are permeable to reaction stream flow. Permeable partitions disposed between zones, such as, mesh screens, expanded metal, reticulated ceramics, or the like, can be provided for this purpose.

All of the reformer reactors 10, 60, 76, and 96 have housings having first zones 18, 62, 78 and 98 for containing reactants in a reactions stream, collection spaces 40, 70, 86, and 112, for collecting product gas, and all have intermediate zones interposed between the first zones and the collection zones. Reaction stream flow paths P1-P4, along with appropriate thermal insulating members, 14, 16, 74, and 120, assist in directing heated reaction stream from the first zones to the collection spaces primarily in a direction coinciding

with the direction of a substantial portion of the overall heat flux out of the reactors.

It should be understood that advantages of the present invention can be achieved for reactors utilizing a flow path directing flow in diverging directions and continuing in the same general directions from a first zone into and through a second zone even though the flow path between other zones in the same reactor may differ. Reference to a "first zone," "second zone," etc. is meant only to identify a particular zone's relative position to adjacent zones of interest.

For example, a first zone does not have to be the first zone or area of significance in the reactor. The designation of "first zone" merely means a zone which is immediately upstream and adjacent to a second zone of interest. To exemplify this, FIG. 7 is provided to schematically disclose a reactor 122 similar to reactor 10; but wherein reactants (reaction stream) initially flow axially (from inlet 121) through a central cylindrical steam-reforming zone 123 of the reactor 122 (as identified generally by arrows 124). Then the reactants turn and flow radially in diverging directions through a constricted transition zone 126 (as indicated by arrows 128). Then the reaction stream flows counter-axially into an annular first zone 129 (as indicated by the arrows 130). Then according to the invention, the reaction stream flows from first zone 129 into and through a second zone 132 and a third zone 134 along a flow path P5. An annular collection space 136 is provided to collect the desired reaction products, with an outlet 138 to direct the reaction products to a desired location.

It should also be understood that "same general direction" intends a focus on the dominant direction of the overall reaction stream flow entering, traversing, and exiting a zone. The phrase is not intended to  
5 include minor and temporary deviations of flow direction through a zone of small, discrete, portions of the reaction stream flowing around small obstructions such as, catalyst granules, heat exchange tubes, and the solid portions of partitions, such as expanded metal or screen  
10 mesh.

While the specific embodiments have been illustrated and described, numerous modifications come to mind without significantly departing from the spirit of the invention and the scope of protection is only limited  
15 by the scope of the accompanying claims.

## CLAIMS

1. A reformer reactor for producing hydrogen gas from hydrocarbons comprising:
  - (a) a first zone;
  - 5 (b) a second zone adjacent the first zone; and,
  - (c) a flow path for directing flow of a reaction stream in diverging directions from the first zone into the second zone, the flow of the reaction stream continuing in the same general diverging directions  
10 through the second zone.
2. The reactor of Claim 1, including at least a third zone adjacent the second zone, the flow path continuing a flow of the reaction stream into and through  
15 the third zone in the same general directions as the reaction stream flowed into and through the second zone.
3. The reactor of Claim 2, including a fourth zone adjacent the third zone, the flow path continuing a  
20 flow of the reaction stream into and through the fourth zone in the same general directions as the reaction stream flowed into and through the second zone.
4. The reactor of Claim 1 wherein the first and  
25 second zones are generally spherical and the flow directions are radially away from the first zone.
5. The reactor of Claim 1 wherein the first and second zones are generally hemispherical and the flow  
30 directions are radially away from a spherical portion of the hemispherical first zone.



6. The reactor of Claim 1 wherein the first and second zones are generally cylindrical and the flow directions are radially away from the first zone.

5           7. The reactor of Claim 1 wherein the first and second zones are generally cylindrical and the flow directions are axially away from the first zone.

8. The reactor of Claim 2 wherein the first,  
10 second, and third zones are generally spherical and the flow directions are radially away from the first zone.

9. The reactor of Claim 2 wherein the first,  
second, and third zones are generally hemispherical and  
15 the flow directions are radially away from a spherical portion of the hemispherical first zone.

10. The reactor of Claim 2 wherein the first,  
second, and third zones are generally cylindrical and the  
20 flow directions are radially away from the first zone.

11. The reactor of Claim 2 wherein the first,  
second, and third zones are generally cylindrical and the  
flow directions are axially away from the first zone.

25

12. The reactor of Claim 3 wherein the first,  
second, third, and fourth zones are generally cylindrical  
and the flow directions are radially away from the first  
zone.

30

13. The reactor of Claim 1 including a first partition separating the first and second zones, the first partition having a plurality of spaced openings to permit the flow of the reaction stream therethrough.

5

14. The reactor of Claim 2 including a first partition separating the first and second zones, and a second partition separating the second and third zones, both the first and second partitions having a plurality  
10 of spaced openings to permit the flow of the reaction stream respectively therethrough.

15. The reactor of Claim 6 including a first partition separating the first and second zones, the  
15 partition having a plurality of spaced openings to permit flow of the reaction stream therethrough.

16. The reactor of Claim 10 including a first partition separating the first and second zones, and a  
20 second partition separating the second and third zones, both the first and second partitions having a plurality of spaced openings to permit the flow of the reaction stream therethrough.

17. The reactor of Claim 13 including:

(a) a partial oxidation reaction vessel being located within the first zone, the vessel having an opening for emission of reactants into the first zone;

5 and,

(b) the number, size, and spacing of the partition openings being selected to control the flow rate and uniformity of the reaction stream from the first zone and into the second zone.

10

18. The reactor of Claim 13 including:

(a) a partial oxidation reaction vessel being located within the first zone, the vessel having an opening for emission of reactants into the first zone;

15 and,

(b) the first partition being constructed of material composition, thickness, and finish to assist in controlling heat transfer between the reaction vessel and the second zone.

20

19. The reactor of Claim 1, wherein:

(a) at the first zone the reaction stream including a partially-oxidized hydrocarbon and hydrogen gas; and,

25

(b) the second zone containing a catalyst.

20. The reactor of Claim 2, wherein:

(a) at the first zone the reaction stream including a partially-oxidized hydrocarbon and hydrogen gas; and,

30

(b) at least one of the second or third zone containing a catalyst.

21. The reactor of Claim 3, wherein:

(a) at the first zone the reaction stream including a partially-oxidized hydrocarbon and hydrogen gas; and,

5 (b) at least one of the second, third, or fourth zones containing a catalyst.

22. The reactor of Claim 6, wherein:

(a) at the first zone the reaction stream including a partially-oxidized hydrocarbon and hydrogen gas; and,

(b) the second zone containing a catalyst.

23. The reactor of Claim 10, wherein:

15 (a) at the first zone the reaction stream including a partially-oxidized hydrocarbon and hydrogen gas; and,

(b) at least one of the second, third, or fourth zones containing a catalyst.

20

24. The reactor of Claim 6 wherein the axial ends of each of the zones have a thermally-insulating member.

25 25. The reactor of Claim 10 wherein axial ends of each of the zones have a thermally-insulating member.

26. The reactor of Claim 22 wherein axial ends of each of the zones have a thermally-insulating member.

30 27. The reactor of Claim 23 wherein axial ends of each of the zones have a thermally-insulating member.

28. The reactor of Claim 10, wherein:

(a) at the first zone the reaction stream including a partially-oxidized hydrocarbon and hydrogen gas; and,

5 (b) at least one of the second or third zone containing a catalyst.

29. The reactor of Claim 12, wherein:

(a) at the first zone the reaction stream including a partially-oxidized hydrocarbon and hydrogen gas; and,

(b) at least one of the second, third, or fourth zones contain a catalyst.

15 30. The reactor of Claim 19 wherein the second zone includes a catalyst suitable for catalyzing a steam reforming reaction in the reaction stream.

20 31. The reactor of Claim 20 wherein the second zone includes a suitable catalyst for catalyzing a steam reforming reaction in the reaction stream, and the third zone contains a suitable catalyst for catalyzing a high-temperature shift reaction in the reaction stream.

25 32. The reactor of Claim 21 wherein the second zone containing a suitable catalyst for catalyzing a steam reforming reaction in the reaction stream, and the third zone containing a suitable catalyst for catalyzing a high-temperature shift reaction in the reaction stream,  
30 and the fourth zone including a suitable catalyst for catalyzing a low-temperature shift reaction in the reaction stream.

33. The reactor of Claim 22 wherein the second zone includes a suitable catalyst for catalyzing a steam reforming reaction in the reaction stream.

5           34. The reactor of Claim 28 wherein the second zone containing a suitable catalyst for catalyzing a steam reforming reaction in the reaction stream, and the third zone containing a suitable catalyst for catalyzing a high-temperature shift reaction in the reaction stream.

10           35. The reactor of Claim 29 wherein the second zone containing a suitable catalyst for catalyzing a steam reforming reaction in the reaction stream, the third zone containing a suitable catalyst for catalyzing a high-temperature shift reaction in the reaction stream, and the fourth zone containing a suitable catalyst for catalyzing a low-temperature shift reaction in the reaction stream.

20           36. The reactor of Claim 13 wherein the first partition is a screen mesh.

25           37. The reactor of Claim 14 wherein the partitions are a screen mesh.

          38. The reactor of Claim 17 wherein the first partition is a screen mesh.

30           39. The reactor of Claim 18 wherein the partition is a screen mesh.

40. The reactor of Claim 1 including a partial oxidation reaction vessel being located within the first zone, the vessel having an opening for emission of partially-oxidized hydrocarbons into the first zone.

5

41. The reactor of Claim 19 including a partial oxidation reaction vessel being located within the first zone, the vessel having an opening for emission of partially-oxidized hydrocarbons into the first zone.

10

42. The reactor of Claim 2, including a reactant feed stream for providing reactants into the reaction stream and means for heat exchange with the reactant feed stream prior to entry of the reactants into the first zone, the means being disposed in at least one of the second or third zones so as to utilize heat from the reaction stream flowing therethrough to preheat the feed stream.

20

43. The reactor of Claim 3, including a reactant feed stream for providing reactants into the reaction stream and means for heat exchange with the reactant feed stream prior to entry of the reactants into the first zone, the means being disposed in at least one of the second, third, and fourth zones so as to utilize heat from the reactant stream flowing therethrough to preheat the feed stream.

25

44. The reactor of Claim 20, including a reactant feed stream for providing reactants into the reaction stream and means for heat exchange with the reactant feed stream prior to entry of the reactants into the first

30

zone, the means being disposed in direct contact with a catalyst in at least one of the second or third zones so as to utilize heat from the reactant stream flowing therethrough and the heat from the catalyst to preheat the feed stream.

45. The reactor of Claim 21, including a reactant feed stream for providing reactants into the reaction stream and means for heat exchange with the reactant feed stream prior to entry of the reactants into the first zone, the means being disposed in the catalyst for direct contact therewith in at least one of the second, third, and fourth zones so as to utilize heat from the reactant stream flowing therethrough and the heat of the catalyst to preheat the feed stream.

46. The reactor of Claim 30 wherein the means for heat exchange with a reactant feed stream also including means for regulating the heat exchange so that a desired thermal gradient can be maintained in the catalyst of the third zone and the reaction stream temperature across the zone wherein the means for heat exchange is disposed.

47. The reactor of Claim 31 wherein the means for heat exchange with a reactant feed stream also having means for regulating the heat exchange so that a desired thermal gradient can be maintained in the catalyst of the third zone and the reaction stream temperature across the zone wherein the means for heat exchange is disposed.

48. The reactor of Claim 32 wherein the means for heat exchange with a reactant feed stream also having



means for regulating the heat exchange so that a desired thermal gradient can be maintained in the catalyst of the third zone and the reaction stream temperature across the zone wherein the means for heat exchange is disposed.

5

49. The reactor of Claim 1 including:

(a) a means for flowing oxygen to the first zone;

(b) a means for flowing a fuel to be oxidized to the first zone; and,

10 (c) a means for cooperating the means for flowing oxygen and the means for flowing fuel such that the flow of fuel assists the flow of oxygen.

50. The reactor of Claim 6 including:

15 (a) a means for flowing oxygen to the first zone;

(b) a means for flowing a fuel to be oxidized to the first zone; and,

(c) a means for cooperating the means for flowing oxygen and the means for flowing fuel such that the flow  
20 of fuel assists the flow of oxygen.

51. The reactor of Claim 10 including:

(a) a means for flowing oxygen to the first zone;

(b) a means for flowing a fuel to be oxidized to  
25 the first zone; and,

(c) a means for cooperating the means for flowing oxygen and the means for flowing fuel such that the flow of fuel assists the flow of oxygen.

30 52. The reactor of Claim 49 wherein the means for cooperating including joining the fuel flow into the oxygen flow downstream of a source of the oxygen and

flowing the fuel at a higher velocity than a velocity of the oxygen upstream of joining the fuel flow.

53. The reactor of Claim 49 wherein the fuel is a hydrocarbon which is a gas at standard temperature and pressures and is delivered to the fuel flow from a pressurized container.

54. The reactor of Claim 49 wherein the means for flowing oxygen includes a first tube, the means for flowing fuel includes a second tube, and the means for cooperating including a union of the first and second tubes such that a spray of fuel can issue from the second tube inside the first oxygen-carrying tube.

55. A reformer reactor for producing hydrogen-rich gas comprising:

(a) a vessel having a first zone for containing a reaction stream with reactants, a collection space for  
5 collecting product gas, at least one intermediate zone interposed between the first zone and the collection space; and,

(b) a means for directing a heated reactant stream from the first zone to the collection space  
10 primarily in the direction coinciding with the direction of a substantial portion of the overall heat flux out of the vessel.

56. The reformer reactor of Claim 55 having three  
15 zones interposed between the first zone and the collection space.

57. The reformer reactor of Claim 56 wherein the second zone containing a suitable catalyst for catalyzing  
20 a steam reforming reaction in a reaction stream, the third zone containing a suitable catalyst for catalyzing a high-temperature shift reaction in a reaction stream, and the fourth zone containing a suitable catalyst for catalyzing a low-temperature shift reaction in a  
25 reaction stream.

58. The reformer reactor of Claim 55 wherein the all of the zones are arranged as nested coaxial cylinders and the vessel including sufficient thermal insulation at  
30 its axial ends such that heat flux and accordingly the reactant flow, is primarily radially outward from the first zone to the collection zone.

59. The reformer reactor of Claim 57 wherein all of the zones are arranged as nested coaxial cylinders and the vessel including sufficient thermal insulation at axial ends of the nested cylinders such that the heat flux, and accordingly the reaction stream flow, is primarily radially outward from the first zone to the collection space.

60. The reformer reactor of Claim 55 including a partial oxidation reactor located in the first zone for issuing a partially-oxidized hydrocarbon reactant mixture to the first zone.

61. The reformer reactor of Claim 59 including a partial oxidation reactor located in the first zone for issuing a partially-oxidized hydrocarbon reactant mixture to the first zone.

62. The reformer reactor of Claim 57 including a partial oxidation reactor located in the first zone for issuing a partially oxidized hydrocarbon reactant mixture to the first zone.

63. A reformer reactor for producing a hydrogen-rich gas comprising:

- (a) a first zone for containing reactants;
- (b) at least one other zone within which the  
5 first zone is nested; and,
- (c) a boundary between each zone, the boundary being permeable to a reaction stream so as to permit flow thereof from the first zone to and through each subsequent zone through the respective boundaries  
10 therebetween.

64. The reformer reactor of Claim 63 having three nested zones around the first zone.

- 15 65. The reformer reactor of Claim 64 wherein the second zone containing a suitable catalyst for catalyzing a steam reforming reaction in the reaction stream, the third zone containing a suitable catalyst for catalyzing a high-temperature shift reaction in the reaction stream,  
20 and the fourth zone containing a suitable catalyst for catalyzing a low-temperature shift reaction in the reaction stream.

- 25 66. The reformer reactor of Claim 63 wherein the first zone is a cylinder and the three subsequent zones are tubular cylinders all nested coaxially and a closure is provided at axial ends of the cylindrical zones, such that the reaction stream flow is primarily radially outward from the first zone to and through the third  
30 zone.

67. The reformer reactor of Claim 64 wherein the first zone is a cylinder and the three subsequent zones are tubular cylinders all nested coaxially and a closure is provided at axial ends of the cylindrical zones, such  
5 that the reaction stream flow is primarily radially outward from the first zone to and through the third zone.

68. The reformer reactor of Claim 63 including a  
10 partial oxidation reactor located in the first zone for issuing a partially-oxidized hydrocarbon reactant mixture to the first zone.

69. The reformer reactor of Claim 65 including a  
15 partial oxidation reactor located in the first zone for issuing a partially-oxidized hydrocarbon reactant mixture to the first zone.

70. The reformer reactor of Claim 67 including a  
20 partial oxidation reactor located in the first zone for issuing a partially oxidized hydrocarbon reactant mixture to the first zone.

FIG. 1

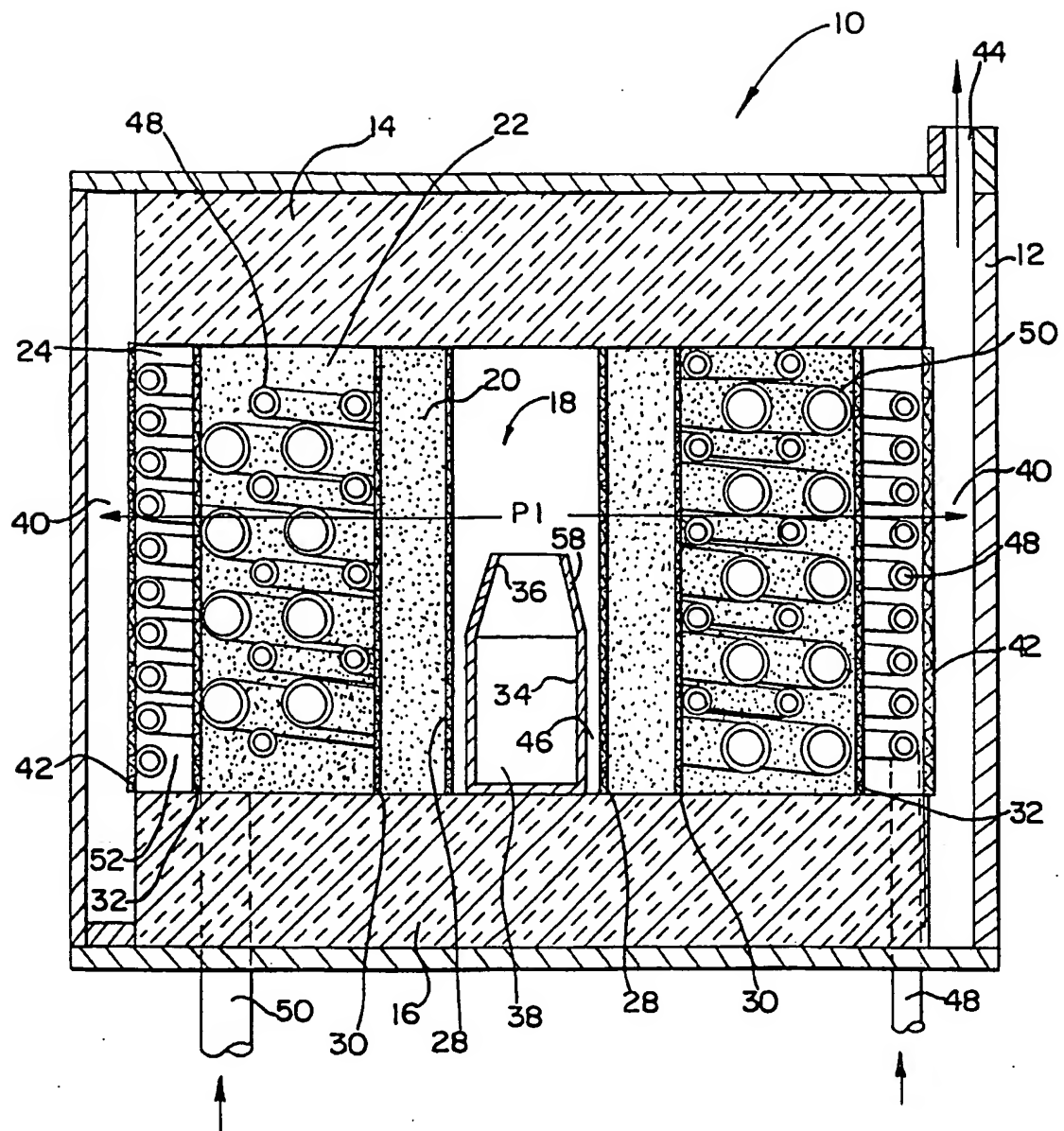


FIG. 2

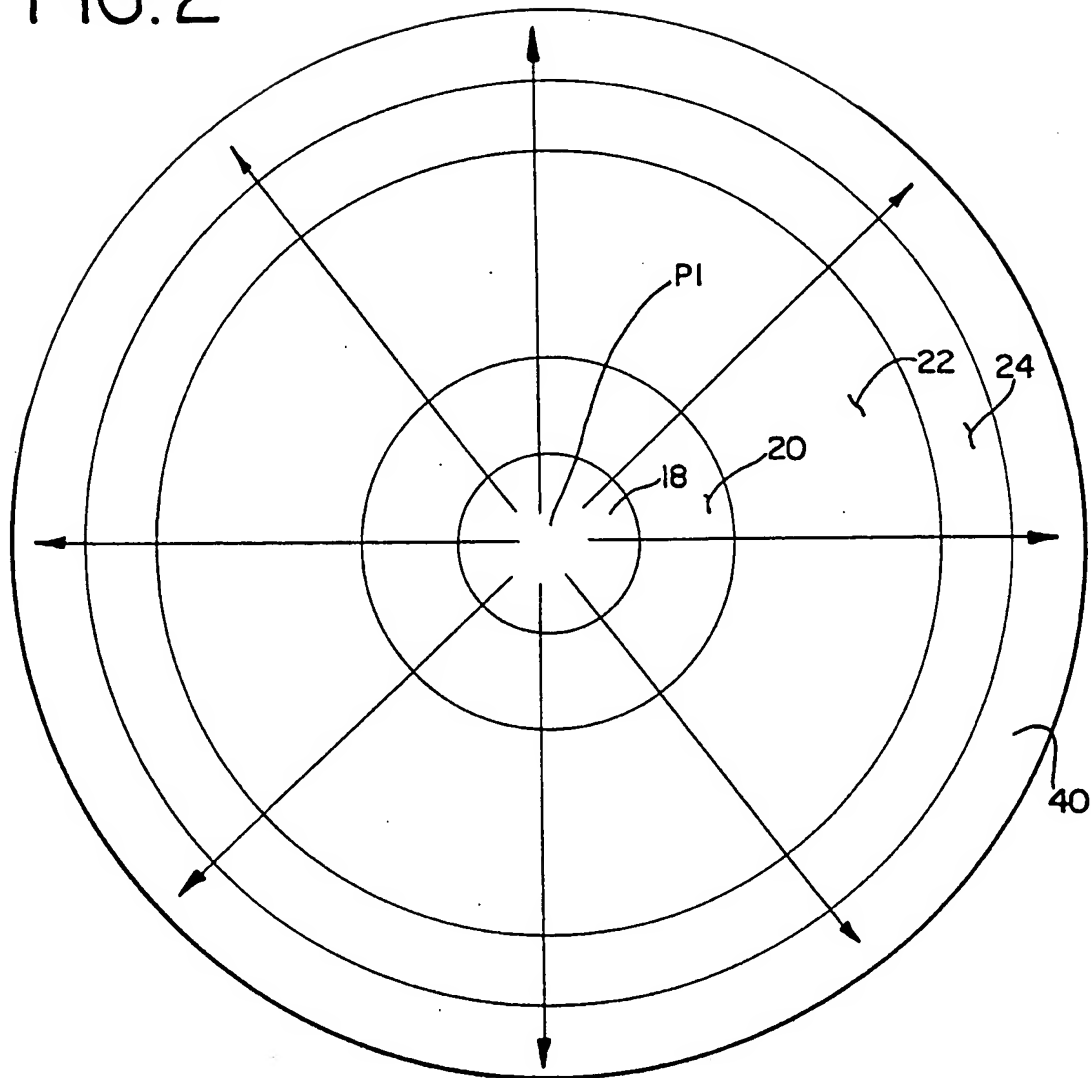


FIG. 3

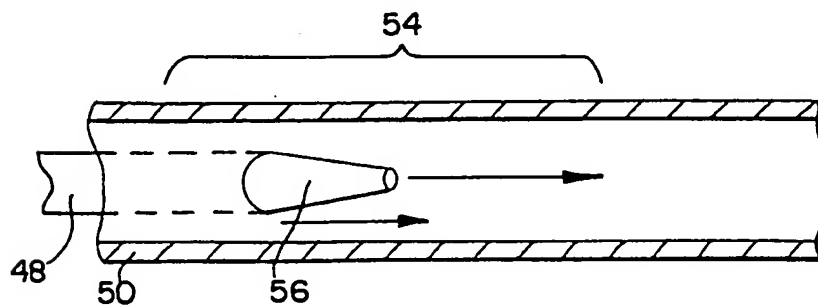




FIG. 4

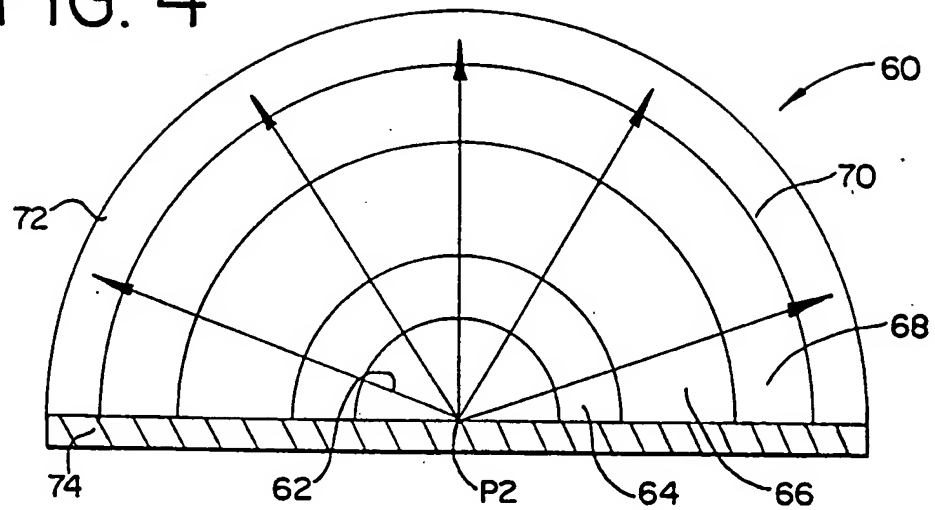


FIG. 5

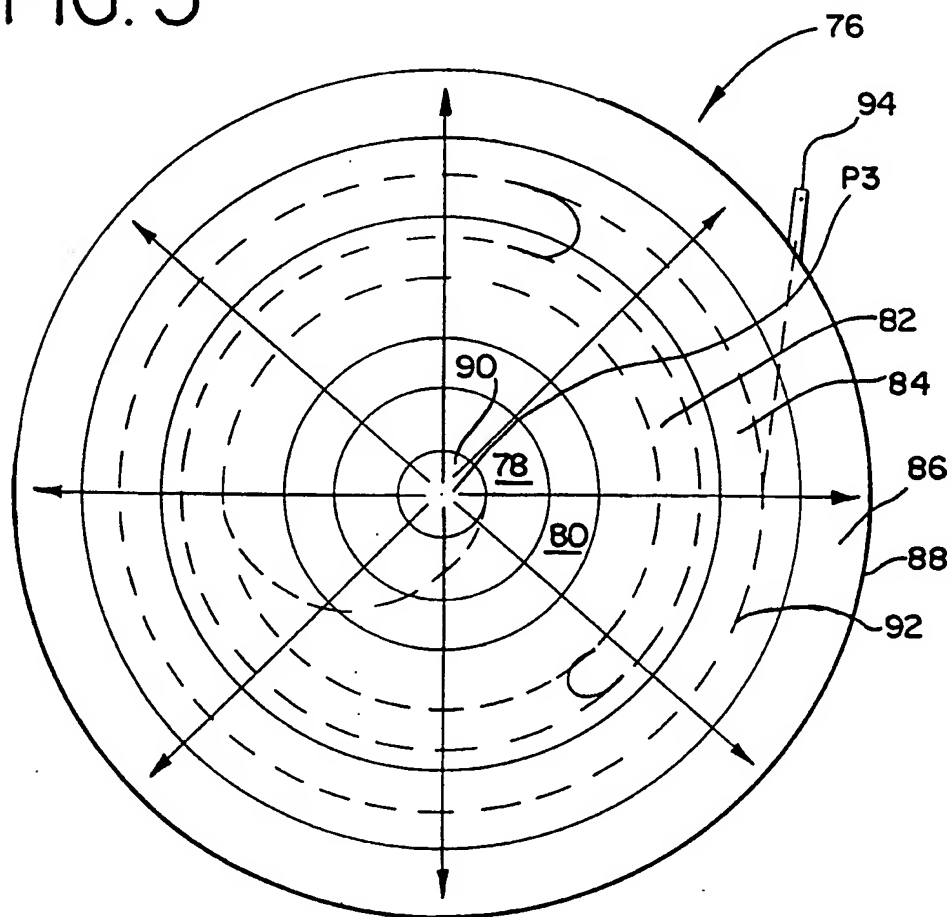


FIG. 6

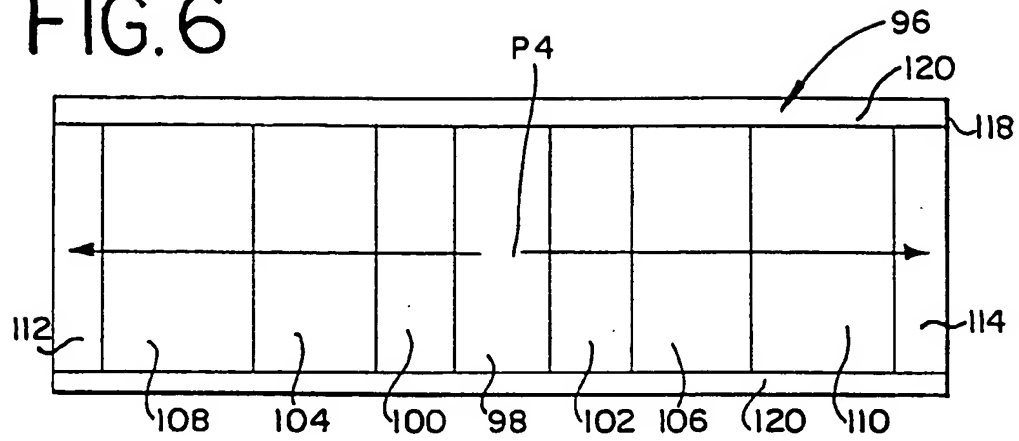
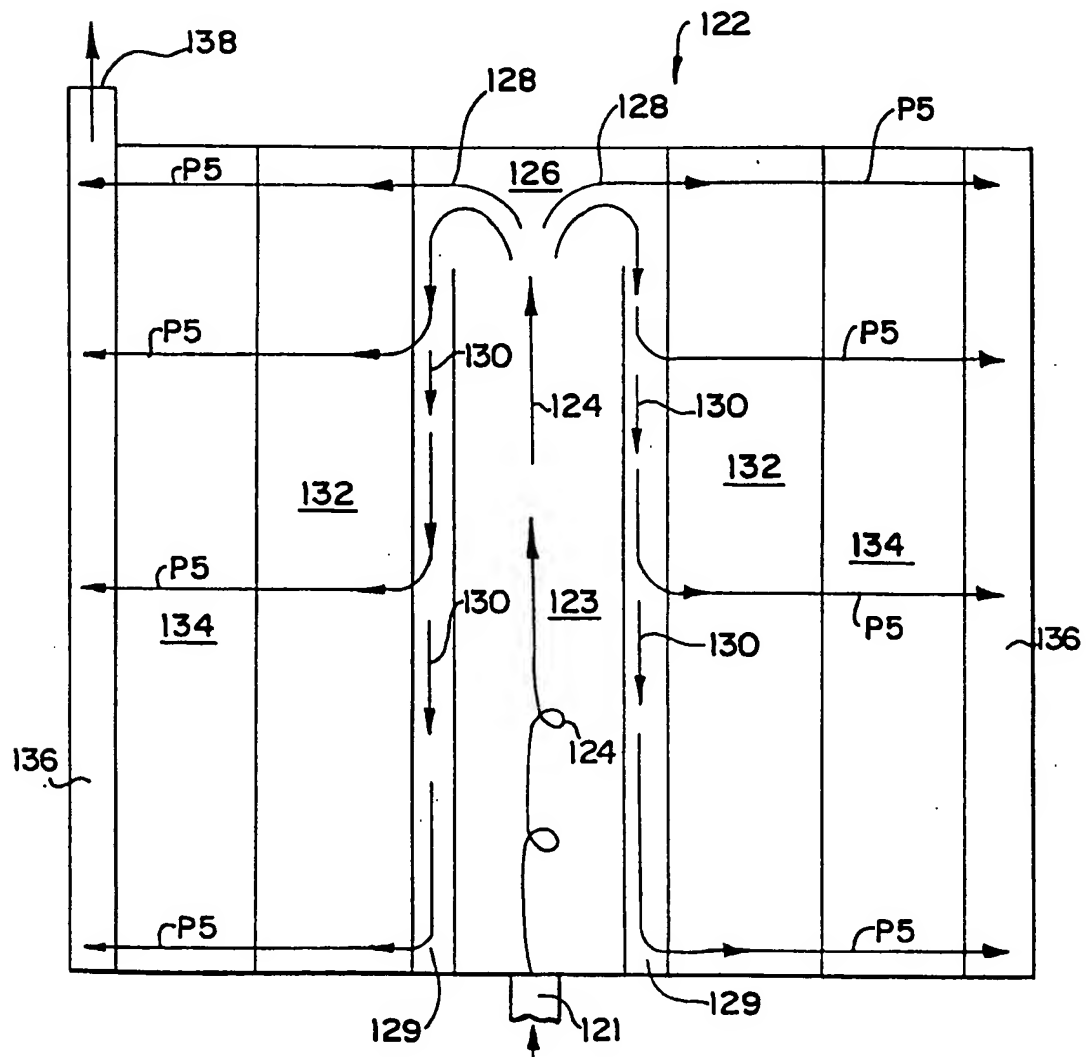


FIG. 7



# INTERNATIONAL SEARCH REPORT

In. :tional Application No  
PCT/US 99/00833

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C01B3/38 C01B3/48 C01B3/32 B01J8/04 B01J8/02 H01M8/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C01B B01J H01M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 37 08 957 A (LINDE AG) 6 October 1988  see column 5, line 28 - line 41; figure 2 ---	1-4,6-8, 10,12, 13,55, 56,63,64
X	EP 0 442 164 A (SHELL INT RESEARCH) 21 August 1991  see claims	1,6,7, 13,22, 36,55,63
A	IDem	17-21, 23,30
X	US 3 733 181 A (TOURTELLOTTE J ET AL) 15 May 1973  see the whole document --- <div style="text-align: center;">-/--</div>	1,6,7, 13,15, 36,55,63
<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
<b>* Special categories of cited documents :</b>		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center;">19 April 1999</div>		Date of mailing of the international search report  <div style="text-align: center;">27/04/1999</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center;">Van der Poel, W</div>

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/00833

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 082 609 A (ICI PLC) 29 June 1983 see the whole document	1,6
A	IDEM	12,43-45
X	DE 39 39 544 A (UHDE GMBH) 6 June 1991 see the whole document	1,4,5
A	US 5 458 857 A (COLLINS ROBERT D ET AL) 17 October 1995 cited in the application  see column 2, line 32 - line 53 see column 5, line 14 - column 8, line 23 see figures	1,6,7, 17-35, 49-51, 55,57, 63,65
A	GB 2 296 719 A (HITACHI LTD) 10 July 1996  see page 11, line 4 - page 15, line 20 see figure 1	1,17-19, 30

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/00833

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 3708957	A	06-10-1988	NONE	
EP 0442164	A	21-08-1991	AU 633675 B	04-02-1993
			AU 6923091 A	11-07-1991
			CA 2033790 A	11-07-1991
			DE 69002452 T	18-11-1993
			DK 442164 T	11-10-1993
			JP 4215835 A	06-08-1992
			NO 176750 B	13-02-1995
US 3733181	A	15-05-1973	DE 2306471 A	29-08-1974
			FR 2217061 A	06-09-1974
			GB 1366061 A	11-09-1974
			NL 7301678 A	08-08-1974
EP 0082609	A	29-06-1983	JP 1726958 C	19-01-1993
			JP 4013020 B	06-03-1992
			JP 58112044 A	04-07-1983
			US 4882444 A	21-11-1989
DE 3939544	A	06-06-1991	CA 2030915 A	31-05-1991
			DE 9000603 U	29-03-1990
			DE 9006659 U	23-08-1990
			DK 432364 T	13-12-1993
			EP 0432364 A	19-06-1991
US 5458857	A	17-10-1995	CA 2109655 A	03-06-1994
			DE 69309862 D	22-05-1997
			DE 69309862 T	24-07-1997
			EP 0600621 A	08-06-1994
			JP 6239601 A	30-08-1994
GB 2296719	A	10-07-1996	JP 8189380 A	23-07-1996
			GB 2305186 A, B	02-04-1997
			US 5873236 A	23-02-1999
			US 5826422 A	27-10-1998